

III.B.2 Development of Ni-Based Sulfur-Resistant Catalyst for Diesel Reforming

Gunther Dieckmann

Chevron Energy Research and Technology Company

100 Chevron Way

Richmond, CA 94802

Phone: (510) 242-2218; Fax: (510) 242-2823; E-mail: ghdi@chevrontexaco.com

DOE Project Manager: Magda Rivera

Phone: (304) 285-1359; E-mail: Magda.Rivera@netl.doe.gov

Objectives

- Reform real sulfur-containing diesel fuels under minimum recycle conditions to produce hydrogen and carbon monoxide for use in solid oxide fuel cells.
- Test utility of radio frequency coke suppression in preventing catalyst aging when reforming diesel fuel containing 50 ppm sulfur.
- Determine the maximum sulfur concentration that the catalyst can handle.
- Develop a commercially viable low-cost sulfur-resistant reforming catalyst.
- Demonstrate that the catalyst can reform a real diesel fuel in long-term aging tests for greater than 3000 hours (in Phase II if approved).

Approach

- Reform a low-sulfur diesel fuel using Chevron's sulfur-resistant reforming catalyst under a minimum recycle gas rate of only 20%. Determine if the catalyst activity is acceptable.
- Increase the sulfur content of the fuel until the catalyst's reforming activity is "strained". In other words, develop a rapid aging test.
- Apply radio frequency coke suppression to improve activity or catalyst life, and then determine the optimum frequency and field strength.
- Optimize the catalyst formulation (in Phase II if approved).
- Perform long-term aging tests in Phase II.

Accomplishments

- Determined that Chevron's low-cost Ni-based reformer catalyst can readily reform a low-sulfur diesel fuel of the type that will be on the market in the United States in 2006.
- Established that 50 ppm S diesel fuel reduces the activity of the catalyst and decreases catalyst life. Coking appears to be leading to catalyst deactivation.
- Demonstrated that Chevron's Ni-based reformer catalyst can adsorb greater than 95% of the sulfur in the feed for the first 1 to 2 hours following regeneration. A two-bed system could be installed to desulfurize/reform low sulfur containing feeds so that the current sulfur-sensitive anode catalyst system can still be used.
- Radio frequency coke suppression appears to improve catalyst activity.

Future Directions

- Continue radio frequency coke suppression experiments.
- Select the most advantageous sulfur-resistant reforming catalyst formulation. If possible, prepare the catalyst in a monolith form.
- Conduct long-term, 3000 hr, aging tests using the optimized catalyst formulation with a real diesel fuel.

Introduction

For diesel, jet or gasoline fuel to be used in a fuel cell, the liquid hydrocarbon fuel must first be reformed into hydrogen and carbon monoxide. Typically, the hydrocarbon fuel is first mixed with a limited amount of air and, in some systems, a small amount of off-gases from the anode of the fuel cell stack to supply steam. The resulting mixture is then passed over a nickel or platinum group metal catalyst to produce hydrogen and carbon monoxide, which are then sent to the fuel cell stack to produce electricity. Reformer catalysts based on low-cost nickel are preferred because they are cheaper to manufacture and more durable than platinum group metal catalysts. Unfortunately, even sub part per million levels of sulfur in the fuel can poison most reformer catalysts, resulting in a product stream with a high concentration of partially reformed hydrocarbons that will coke or foul most anode catalysts used in fuel cell stacks.

Thus, Chevron, Argonne National Laboratory, and the National Energy Technology Laboratory at Morgantown are developing Ni-based (low-cost) reforming catalysts that can tolerate the levels of sulfur found in reformulated gasoline or in low-sulfur 2006 diesel fuel. Developing a sulfur-resistant reforming catalyst is a far better approach than trying to adsorb the complex sulfur compounds found in the various fuels in a separate system prior to reforming, since most sulfur compounds found in severely hydrotreated diesel are not easily adsorbed, and many of the proposed adsorbents are pyrophoric. The Chevron catalyst has the ability to reform heavy hydrocarbons (including aromatics) found in diesel fuel while also adsorbing sulfur. After reforming, the feed sulfur is transformed into hydrogen sulfide, which can be easily adsorbed. This type of dual functional catalyst is currently needed, since the anode catalysts in solid oxide fuel cells and molten carbonate fuel cells are also based on nickel and are

poisoned by sulfur. In the future, if sulfur-resistant anode catalysts are successfully developed, the requirement for sulfur adsorption can be dropped; however, the reforming catalyst will still need to resist sulfur poisoning.

Approach

We have found that the most serious problem with development of a sulfur-resistant reforming catalyst is coking, and that Ni-based catalysts tend to coke more than platinum group metal-based catalysts. However, Ni-based catalysts are preferred not only because they are significantly cheaper, but also because they are more durable. Both of these issues are critical in ultimately developing a viable auxiliary power unit with a cost of less than \$400/kW. Not only does coke block catalytic sites, leading to the production of undesirable heavy hydrocarbons that will coke or foul anode catalysts, it also leads to aging of the catalyst due to metal stripping. To minimize coke production on the catalyst, we first focused on optimizing the pilot plant design, introduced the use of detergents in the fuel to prevent fuel pulsing in the orifice [1], and applied a radio frequency electromagnetic field to the reformer catalyst bed to suppress metal-catalyzed coking [2]. Most of Phase I of this project is aimed at understanding the frequency and electric field strength effects on reforming catalyst activity and life. Phase II of this project (if approved) will be directed towards optimizing the catalyst formulation (there are a number of competing formulas), developing a monolith version of the catalyst, and performing a long-term (3000+ hours) aging test.

Results

Our first achievement was to demonstrate that a real 7 ppm sulfur containing diesel fuel purchased at a filling station was easily reformed over Chevron's Ni-based reformer catalyst at an oxygen-to-carbon ratio of 1.0 using a minimum simulated 20% recycle

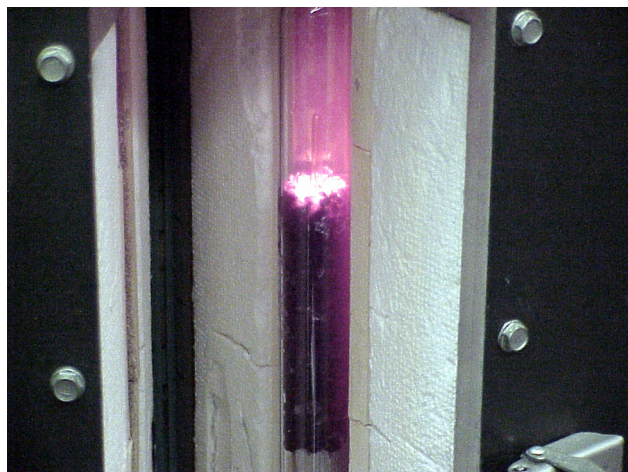


Figure 1. Low-Sulfur Diesel Is Reformed over Chevron's Catalyst

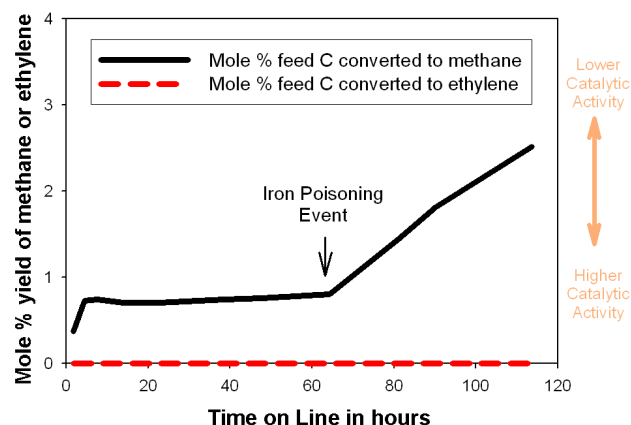


Figure 2. Catalytic Activity of Chevron's Catalyst Reforming a 7 ppm S Diesel Fuel

stream consisting of steam in nitrogen gas (H_2O -to-C ratio of 0.2). This fuel is representative of a low-sulfur diesel fuel that will be available in the U.S. market in 2006. Figure 1 shows the flame front of the reformer catalyst bed. In order to maximize performance, it is absolutely critical that this flame front remain steady and even with time. Figure 2 shows the yield of methane and higher hydrocarbons as a function of time on line. Chevron's sulfur-resistant catalyst easily reformed the fuel, producing only a tiny amount of methane. No higher hydrocarbon species such as ethylene, propylene or higher were produced that could potentially foul an anode catalyst in a fuel cell stack. The reformer catalyst appeared very stable for at least the first 60 hours. It is important to understand that the catalyst was regenerated every 8 to 10 hours by stopping the

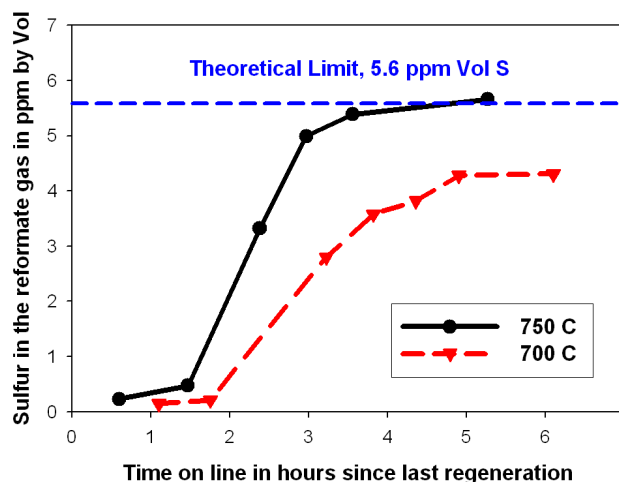


Figure 3. Concentration of Sulfur in the Reformat Gas Stream from Reforming a 50 ppm S Diesel Fuel at Two Different Temperatures

feed and allowing the air to burn off any deposited coke, as well as strip away the adsorbed sulfur as SO_x . Chevron's catalyst was then rapidly activated (i.e., the Ni was reduced) in a matter of seconds once the fuel was started again. There was a one-time incident at around 60 hours on line, where iron was accidentally deposited onto the front part of the catalyst bed (360 ppm Fe). This resulted in deactivation of the catalyst due to metal-catalyzed coking. Apparently, under these low steam conditions, iron makes coke (at least on this particular catalyst). It is not clear at this point in time if the other alternative sulfur-resistant reforming catalysts will be as sensitive to iron poisoning. As a consequence, the pilot plant was rebuilt to remove any potential source of iron. In real commercial reformers, great care will need to be taken in selecting metallurgy [3] and in process design to avoid upstream metal-catalyzed coking incidents that may deposit iron on the reformer catalyst if this turns out to be a general problem.

Given the early success of reforming a real low-sulfur diesel fuel, the project objectives were modified to focus on reforming a higher 50 ppm S diesel fuel with and without radio frequency coke suppression.

Figure 3 shows the concentration of sulfur (as hydrogen sulfide) in the reformat gas produced at 750°C or 700°C by reforming a 50 ppm S diesel fuel over slightly aged (50 hours) Chevron catalyst. This

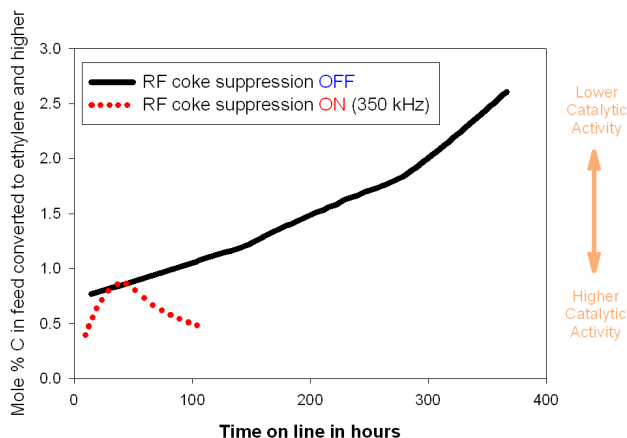


Figure 4. Catalytic Activity and Aging of Chevron's Catalyst Reforming a 50 ppm S Diesel Fuel with and without Radio Frequency (RF) Coke Suppression

graph shows that for the first 1 to 2 hours, greater than 95% of the sulfur is adsorbed by the catalyst. Past this point in time, the adsorptive capacity is reached. Since the breakthrough curve should be a function of the sulfur content of the fuel, a real 2006 diesel fuel with less than 15 ppm S should show sulfur breakthrough after more than 6 hours on line. It is interesting to note that the Chevron catalyst continues to reform the diesel fuel long after sulfur has broken through the bed, indicating that the two functions are separate.

Figure 4 shows that reforming a 50 ppm sulfur containing feed in contrast to 7 ppm S fuel (see Figure 2) produces non-methane hydrocarbons (such as ethylene, propylene, and higher) that have the potential of fouling Ni-based anode catalysts in solid

oxide fuel cells, and that the concentration of these compounds increases as a function of time as the catalyst ages. However, if the catalyst bed is exposed to a radio frequency field of 350 kHz, the amount of coke produced on the catalyst is dramatically reduced, and for the short period of time that we have run the current experiment, it appears to be yielding beneficial results. We will need to run the experiment for the full 300 to 400 hours to be really certain if radio frequency coke suppression is working.

Conclusions

Chevron's current sulfur-resistant reformer catalyst is capable of reforming low-sulfur reformulated gasoline and low-sulfur diesel fuels that are available or will soon be available in the United States and Europe. When fresh, Chevron's catalyst can be used to adsorb the sulfur from the feed to produce very low sulfur (<0.20 ppm vol) reformat gas that can be fed directly to a solid oxide fuel cell with a Ni-based anode catalyst.

FY 2005 Publications/Presentations

1. "Development of Ni-Based Sulfur Resistant Catalyst for Diesel Reforming", G. H. Dieckmann, Presented at the SECA Core Technology Peer Review Workshop, Tampa, Florida, January 27, 2005

References

1. U.S. Patent 6,660,050
2. U.S. Patent 6,790,547
3. U.S. Patent 6,803,029